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A Kinetic Study on the Proton-transfer Reactions of Bis(dimethylglyoximato)cobalt(III) Complex Ions in Dioxane-Water Media†

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The proton-transfer reactions of bis(dimethylglyoximato)cobalt(III) complex ions, $[Co^{III}(dmgH)_2X_2]^n$, with hydroxide ion, OH^-, were studied in dioxane–water media by means of a temperature-jump method. The rate constant, k_f, for the direct proton-transfer from $[Co^{III}(dmgH)_2X_2]^n$ to OH^- was found to be 1.6×10^5—2.9×10^6 $mol^{-1}\,dm^3\,s^{-1}$ in aqueous solution. The value of k_f for $[Co^{III}(dmgH)_2(CN)_2]^-$ anion decreased gradually from 1.6×10^5 to 4.0×10^4 $mol^{-1}\,dm^3\,s^{-1}$ for the change in the mole fraction of dioxane, x_{diox}, from 0 to 0.174. On the other hand, with increase in x_{diox}, the value of k_f for $[Co^{III}(dmgH)_2(NH_3)_2]^+$ cation gradually decreased from 2.9×10^6 to 1.1×10^6 $mol^{-1}\,dm^3\,s^{-1}$ in a region of lower x_{diox}, and then increased from 1.1×10^6 to 1.6×10^7 $mol^{-1}\,dm^3\,s^{-1}$ in a region of higher x_{diox}. The dependence of k_f on x_{diox} is interpreted in connection with reaction mechanism.

A large number of fast proton-transfer reactions in aqueous solutions have been investigated by relaxation techniques,[1] but only a few measurements have been reported for the reactions in non-aqueous media such as dioxane–water,[2–5] DMSO–water,[6] chlorobenzene,[7] and acetonitrile.[8]

We have studied the proton-transfer reactions of the univalent[4] and bivalent[5] anions of *o*-hydroxy azo compounds with hydroxide ion in dioxane–water media using a temperature-jump method. From the change in k_f of these Brønsted acids with increasing x_{diox} the dependency of k_f on x_{diox} was explained by both the change of the dielectric constant of medium and the solute-solvent interactions.

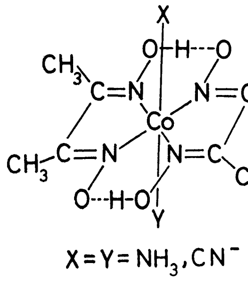

Fig. 1. Structural formulae of $[Co^{III}(dmgH)_2XY]^n$.

It has been established that dimethylglyoxime ($dmgH_2$) forms a stable square planar complex, $[Co^{III}(dmgH)_2X_2]Y$, on the basis of NMR[9] and IR[10] spectroscopic studies, chemical characteristics,[11] and syntheses,[12] where dmgH, X, and Y denote the coordinated univalent dimethylglyoximate anion, the axial ligand, and the counter ion, respectively. The structure of complexes having axial ligands is shown in Fig. 1. They constitute a series which enables us to design systematic variations in acid-dissociation constant and charge type of complexes. The acid-dissociation of bis(dimethylglyoximato)cobalt(III) complex ions can generally be represented by

$$[Co^{III}(dmgH)_2X_2]^n \rightleftarrows [Co^{III}(dmg)(dmgH)X_2]^{n-1} + H^+, \qquad (1)$$

where dmg denotes the coordinated bivalent dimethylglyoximate anion.[13,14] The values of pK_a of these weak Brønsted acids are in the order of magnitude 10—12 due to the strong intramolecular hydrogen-bond, $OH\cdots O^-$.

In the present paper, we report a kinetic study on the proton-transfer reactions in dioxane–water media of diamminebis(dimethylglyoximato)cobalt(III) cation ($[Co^{III}(dmgH)_2(NH_3)_2]^+$; DGA cation) and dicyanobis(dimethylglyoximato)cobaltate(III) anion ($[Co^{III}(dmgH)_2(CN)_2]^-$; CDG anion). DGA cation and CDG anion are relatively stable in both aqueous and dioxane–water media. The values of pK_a were determined spectrophotometrically (pK_a^c(s)) and kinetically (pK_a^c(k)), the pK_a^c(s) and pK_a^c(k) values being in good agreement with each other at each dioxane content. The rate constants, k_f and k_r, for the reaction

$$[Co^{III}(dmgH)_2X_2]^n + OH^- \underset{k_r}{\overset{k_f}{\rightleftarrows}} [Co^{III}(dmg)(dmgH)X_2]^{n-1} + H_2O \qquad (2)$$

were measured by the temperature-jump method. The dependency of the value of k_f on x_{diox} was found to differ considerably from each other due to the difference in the signs of their charge and the solute-solvent interactions. The dependency is discussed in connection with reaction mechanism.

Experimental

Materials. Water was deionized and distilled. Guaranteed grade dioxane (Wako) was distilled over sodium.

Bis(dimethylglyoximato)diamminecobalt(III) chloride, $[Co^{III}(dmgH)_2(NH_3)_2]Cl\cdot5H_2O$, was prepared from purpureo salt, $[Co^{III}Cl(NH_3)_5]Cl_2$, and dimethylglyoxime in the presence of ammonium acetate, and recrystallized from hot water.[15] Found: C, 21.28; H, 6.78; N, 18.90; Cl, 7.77%. Calcd for $C_8H_{30}N_6O_9CoCl$: C, 21.41; H, 6.74; N, 18.73; Cl, 7.90%.

Potassium dicyanobis(dimethylglyoximato)cobaltate(III), $K[Co^{III}(dmgH)_2(CN)_2]\cdot3/2\cdot H_2O$, was prepared from $[Co^{III}(dmgH)_2(NH_3)_2]Cl\cdot5H_2O$ and potassium cyanide.[16] Found: C, 28.30; H, 3.97; N, 19.86%. Calcd for $K[Co(C_8H_{14}O_4N_4)(CN)_2]\cdot3/2\cdot H_2O$: C, 29.49; H, 3.96; N, 20.63%.

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The metal complex $[Co^{III}(dmgH)_2(NH_3)_2]Cl$ at pH 4.3—9.5 was strongly adsorbed on the cation-exchange resin (Dowex 50W-X8) but not on the anion-exchange resin (Dowex 1-X4), indicating that the metal complex exists in a cationic form at pH 4—9. In the pH region higher than 10.17, the pK_a^c of the complex, a neutral species, $[Co^{III}(dmg)(dmgH)(NH_3)_2]$ is formed. On the other hand, the metal complex $K[Co^{III}(dmgH)_2(CN)_2]$ at pH 4.0—8.0 was strongly adsorbed on the anion-exchange resin but not on the cation-exchange resin.

Measurements. Measurements of pH in dioxane–water media were reported in a previous paper.[2] The acid-dissociation constants were determined spectrophotometrically with a Hitachi recording spectrophotometer Model EPS-3T. Kinetic measurements were carried out with a Union Giken co-axial-cable temperature-jump apparatus Model RA-105. The reactions were followed on the screen of an oscilloscope Tektronix Type 545B at a wavelength in the range 400—500 nm. All the measurements were carried out at 25.0±0.1 °C and at a constant ionic strength 0.10 adjusted with potassium nitrate.

Results and Discussion

The metal complex ions (Fig. 1) have two equivalent strong intramolecular hydrogen-bonds, $OH\cdots O^-$. An infrared absorption band around 1775 cm^{-1} for $Ni(dmgH)_2$ complex has been assigned to an intramolecular hydrogen bonding.[17] The absorption band for O–H stretching appears at 3170 cm^{-1} in the free ligand dimethylglyoxime. The bond length of the intramolecular hydrogen-bond, $OH\cdots O^-$, was reported to be 2.44 Å from the data of X-ray crystallography.[18] In some $[Co^{III}(dmgH)_2XY]$ complexes the O–H stretching frequency lies in the range 1770—1680 cm^{-1}.[19] As regards the complexes with X, Y=NH_3, a planar chelate structure was confirmed based on the data of X-ray crystallography.[20]

The absorption spectra of an aqueous solution of the cationic complex DGA at various pH values, at 25 °C, and at I=0.1 mol dm^{-3} ($NaClO_4$),[21] gave an isosbestic point at 246 nm (Fig. 2), indicating that the presence of only two absorbing species involved. In the pH region studied only one proton is dissociated from the Co(III) complex ion. The first acid-dissociation constant, $K_a^c(s)$, of the reaction for DGA cation

$$[Co^{III}(dmgH)_2(NH_3)_2]^+ \rightleftharpoons [Co^{III}(dmg)(dmgH)(NH_3)_2]^0 + H^+, \quad (3)$$

and that for CDG anion

$$[Co^{III}(dmgH)_2(CN)_2]^- \rightleftharpoons [Co^{III}(dmg)(dmgH)(CN)_2]^{2-} + H^+, \quad (4)$$

are determined by the change in absorbance at 285 nm, ΔA_{285}, the equilibrium concentration of proton, $\bar{C}_H$, and the total concentration of the complex ion, C.[5] The plot of $C/\Delta A_{285}$ against $\bar{C}_H$ gives a straight line at each solvent composition. The values of $K_a^c(s)$ determined spectrally at various dioxane contents are summarized in Table 1. The value of $pK_a^c(s)$ increases with the increase in x_{diox} irrespective of the difference in the sign of the charge of DGA cation and CDG anion (Fig. 3). The values of $pK_a^c(s)$ of CDG anion at x_{diox}=0 and 0.174 are 1.53 and 2.79 larger than those of DGA cation, respectively. These differences in $pK_a^c(s)$ are attributed to the difference in the basicity of the axial ligands, NH_3 and CN^-.

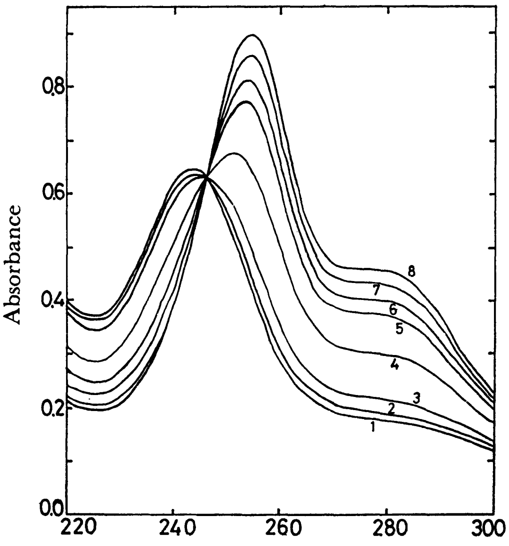

Fig. 2. Absorption spectra of the solution containing 2.59×10^{-5} mol dm^{-3} $[Co^{III}(dmgH)_2(NH_3)_2]^+$ ion at 25 °C and I=0.1 mol dm^{-3} ($NaClO_4$).
pH: (1) 5.85; 6.70, (2) 9.02, (3) 9.33, (4) 10.07, (5) 10.45, (6) 10.75, (7) 10.96, and (8) 11.11.

Table 1. Acid-dissociation constants of $[Co^{III}(dmgH)_2(CN)_2]^-$ and $[Co^{III}(dmgH)_2(NH_3)_2]^+$ in dioxane–water media at 25 °C and I=0.1 mol dm^{-3} ($NaClO_4$)

x_{diox}	$pK_a^c(s) = -\log(K_a^c(s)/\text{mol dm}^{-3})$	
	CDG	DGA
0.000	11.70	10.17[a]
0.023	12.13	10.39
0.050	12.67	10.59
0.083	13.13	10.76
0.128	13.62	11.05
0.174	13.96	11.17

a) This value was reported to be 10.5 at room temperature, see Ref. 13.

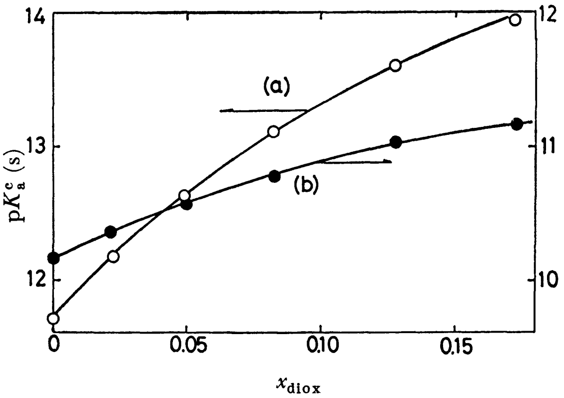

Fig. 3. Dependence of $pK_a^c(s)$ on x_{diox} at 25 °C and I=0.1 mol dm^{-3} ($NaClO_4$).
(a): $[Co^{III}(dmgH)_2(CN)_2]^-$ anion. (b): $[Co^{III}(dmgH)_2(NH_3)_2]^+$ cation.

TABLE 2. RATE AND EQUILIBRIUM CONSTANTS FOR THE PROTON-TRANSFER REACTIONS OF $[\mathrm{Co^{III}(dmgH)_2(CN)_2}]^-$ AND $[\mathrm{Co^{III}(dmgH)_2(NH_3)_2}]^+$ IN DIOXANE–WATER MEDIA AT 25 °C AND $I=0.1$ mol dm^{-3} (KNO_3)

x_{diox}	k_f/mol^{-1} dm^3 s^{-1}	k_r'/s^{-1}	K_b^c/mol^{-1} dm^3	pK_a^c (k)	k_f/mol^{-1} dm^3 s^{-1}	k_r'/s^{-1}	K_b^c/mol^{-1} dm^3	pK_a^c (k)
	CDG				DGA			
0.000	1.6×10^5 a)	1.3×10^3	120	11.66	2.9×10^6 b)	6.0×10^2	4.8×10^3	10.1
0.023	1.3×10^5	2.1×10^3	62	12.26	1.1×10^6	3.4×10^2	3.2×10^3	10.5
0.050	9.5×10^4	2.0×10^3	48	12.59	1.3×10^6	1.6×10^2	8.1×10^3	10.4
0.083	7.0×10^4	2.0×10^3	35	13.00	1.1×10^6	1.2×10^2	9.2×10^3	10.6
0.128	6.5×10^4	2.1×10^3	31	13.48	5.1×10^6	3.0×10^2	1.7×10^4	10.7
0.174	4.0×10^4	1.3×10^3	31	13.82	1.6×10^7	9.0×10^2	1.8×10^4	11.1

a, b) See Ref. 28.

For the proton-transfer reactions in the dioxane–water media of DGA cation,[22)]

$$[\mathrm{Co^{III}(dmgH)_2(NH_3)_2}]^+ + \mathrm{OH^-} \rightleftharpoons [\mathrm{Co^{III}(dmg)(dmgH)(NH_3)_2}]^0 + \mathrm{H_2O} \qquad (6)$$

and those of CDG anion,[23)]

$$[\mathrm{Co^{III}(dmgH)_2(CN)_2}]^- + \mathrm{OH^-} \rightleftharpoons [\mathrm{Co^{III}(dmg)(dmgH)(CN)_2}]^{2-} + \mathrm{H_2O}, \qquad (8)$$

the observed relaxation time, τ, is expressed by

$$\tau^{-1} = k_f(\bar{C}_{\mathrm{H_2A}} + \bar{C}_{\mathrm{OH}}) + k_r', \qquad (8)$$

where $\bar{C}$, suffix H_2A, and k_r' denote the equilibrium concentration, the acid form of Co(III) complex ions, and $k_r[\mathrm{H_2O}]$, respectively. The plot of τ^{-1} against the sum of equilibrium concentrations gives a straight line at each dioxane content (Fig. 4). The values of k_f and k_r thus obtained are summarized in Table 2. The values of k_f are several orders of magnitude smaller than those for the diffusion-controlled proton-transfer reactions due to the strong intramolecular hydrogen-bond, OH···O⁻. The values of log k_f of DGA cation are 1.26 and 2.60 larger than those of CDG anion at $x_{\mathrm{diox}}=0$ and 0.174, respectively. The rate constant for the recombination of CDG anion with OH⁻ ion, k_f, decreases linearly with the increase in x_{diox}, *viz.*, from 1.6×10^5 to 4.0×10^4 mol^{-1} dm^3 s^{-1} for the change in x_{diox} from 0 to 0.174, similar to the changes observed in the univalent anions of *o*-hydroxy azo compounds.[4)] However, the value of k_f of DGA cation decreases in a region of lower x_{diox} from 2.9×10^6 to 1.1×10^6 mol^{-1} dm^3 s^{-1} and increases in a region of higher x_{diox} from 1.1×10^6 to 1.6×10^7 mol^{-1} dm^3 s^{-1}.

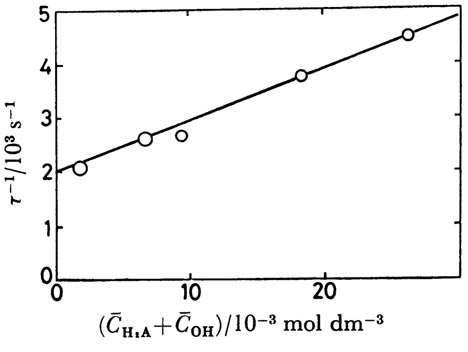

Fig. 4. Plot of the reciprocal relaxation time *vs.* $\bar{C}_{\mathrm{H_2A}}+\bar{C}_{\mathrm{OH}}$ at $x_{\mathrm{diox}}=0.050$, 25 °C, and $I=0.1$ mol dm^{-3} (KNO_3). $[\mathrm{Co^{III}(dmgH)_2(CN)_2}]^-$–$\mathrm{OH^-}$ system.

The value of pK_a^c (k) was evaluated by the relationship, $K_a^c(\mathrm{k}) = (k_f/k_r')\cdot K_w^c = K_b^c\cdot K_w^c$, where K_w^c denotes the apparent ionic product of water.[5)] The values of pK_a^c (k) are summarized in Table 2.

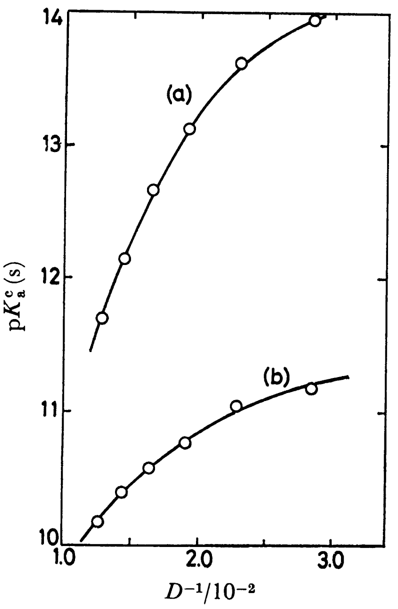

Fig. 5. Dependence of pK_a^c (s) on the inverse dielectric constant of the medium, D^{-1}.
(a): $[\mathrm{Co^{III}(dmgH)_2(CN)_2}]^-$ anion. (b): $[\mathrm{Co^{III}(dmgH)_2(NH_3)_2}]^+$ cation.

In Fig. 5 the values of pK_a^c (s) are plotted against D^{-1}, the inverse macroscopic dielectric constant of the medium. The dependence is not linear. A simple Born-type electrostatic effect is not observed. According to the Born theory[24)] the change in pK_a^c of a Brønsted acid, H_2A, is expressed as

$$\begin{aligned}\Delta\mathrm{p}K_a^c &= \mathrm{p}K_a^c\,(\text{in dioxane–water}) - \mathrm{p}K_a^c\,(\text{in aqueous solution})\\ &= (0.215Ne^2/RT)(1/r_{\mathrm{H}} + Z_{\mathrm{HA}}^2/r_{\mathrm{HA}}\\ &\quad - Z_{\mathrm{H_2A}}^2/r_{\mathrm{H_2A}})(1/D_{\mathrm{II}} - 1/D_{\mathrm{I}}),\end{aligned} \qquad (9)$$

where Z_{HA} and $Z_{\mathrm{H_2A}}$ denote the charge of the base (HA) and the acid form (H_2A), D is the macroscopic dielectric constant of the medium, r the radius of the species, R the gas constant, T the absolute temperature, e the elementary charge, and N the Avogadro number. From

Eq. 9 ΔpK_a^c of the univalent cation ($Z_{H_2A}=+1$ and $Z_{HA}=0$) is expected to be small. However, in the case of DGA cation the value of ΔpK_a^c(s) is as large as 1.00 for the change in x_{diox} from 0 to 0.174. The corresponding value of ΔpK_a^c(s) of CDG anion is 2.26. The value of ΔpK_a^c(s) of univalent anions of *o*-hydroxy azo compounds, 4-(2-hydroxy-5-ethylphenylazo)benzenesulfonic acid (HEB) and 4-(2-pyridylazo)resorcinol (PAR), were reported to be +1.77 and +1.83⁵⁾ and bivalent anions of *o*-hydroxy azo compounds, 4-(2,4-dihydroxyphenylazo)benzenesulfonic acid (TPO) and 7-hydroxy-8-phenylazo-1,3-naphthalenedisulfonic acid (HPN), +2.27 and +2.31.⁴⁾

A reaction mechanism

$$H_2A \underset{k_{21}}{\overset{k_{12}}{\rightleftarrows}} H_2A^* \qquad (10)$$

$$H_2A^* + OH^- \underset{k_{32}}{\overset{k_{23}}{\rightleftarrows}} H_2A^*\cdots(H_2O)_n\cdots OH^- \qquad (11)$$

$$H_2A^*\cdots(H_2O)_n\cdots OH^- \underset{k_{43}}{\overset{k_{34}}{\rightleftarrows}} HA + H_2O, \qquad (12)$$

postulated previously⁵⁾ for the proton-transfer reactions of *o*-hydroxy azo compounds in dioxane–water media might be applied also to those of DGA cation and CDG anion. Equation 10 denotes the equilibrium between two isomeric Co(III) complex ions, *viz.*, an H_2A species having an intramolecular hydrogen-bond and an intermediate species H_2A^* having no intramolecular hydrogen-bond. The rate constant for the recombination of Brønsted acid with OH^-, k_f, is expressed as the product of the rate constant, k_{23}, for the diffusion-controlled encounter between H_2A^* and OH^-, and the equilibrium constant, $K_{12}=[H_2A^*]/[H_2A]$, for the breaking of the intramolecular hydrogen-bond and the interaction with the surrounding water molecules.⁵⁾

$$k_f = K_{12}k_{23} = (k_{12}/k_{21})k_{23} \qquad (13)$$

As regards the ion-ion reactions the Christiansen-Scatchard equation is proposed²⁵⁾

$$\ln(k_f/k_f^\circ) = -z_i z_j e^2/kTr^{\neq}D, \qquad (14)$$

where k is the Boltzmann's constant, $r^{\neq}$ the reaction distance, and k_f° the rate constant at infinite dielectric constant.

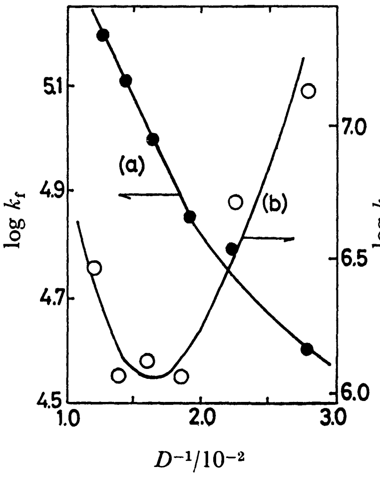

Fig. 6. Dependence of log k_f on the inverse dielectric constant of the medium, D^{-1}.
(a): $[Co^{III}(dmgH)_2(CN)_2]^-$ anion. (b): $[Co^{III}(dmgH)_2(NH_3)_2]^+$ cation.

Since the proton-transfer reaction of CDG anion and OH^- ion is a reaction between the same charge-type ions, the negative slope is expected in the plot of log k_f against D^{-1} (Fig. 6). From the slope the value of $r^{\neq}$ is calculated to be 4.6 Å. This value is the intermediate one between the values for the slightly water-soluble Brønsted acid, (4-(*p*-nitrophenylazo)resorcinol; $r^{\neq}=$ 2.9 Å)³⁾ and a water-soluble Brønsted acid (4-(2-hydroxy-5-ethylphenylazo)benzenesulfonic acid; $r^{\neq}=7.2$ Å).⁴⁾ In the case of CDG anion having hydrophobic groups (four methyl groups) as in 4-(*p*-nitrophenylazo)-resorcinol (one nitro group), the inflection is observed in the plot as shown in Fig. 6.

The following reaction mechanism is proposed for the case of intramolecularly hydrogen-bonded dicarboxylic acid monoanions, AH^-, in aqueous solution.²⁶⁾

$$AH^- + OH^- \rightleftarrows A^-\cdots H\cdots OH^- \rightleftarrows A^{2-} + H_2O, \qquad (15)$$

where $A^-\cdots H\cdots OH^-$ denotes an encounter complex with a weakened intramolecular hydrogen-bond. The mechanism shown in Eqs. 10—12 would be reasonable for the explanation of the solvent effects. From Eq. 14 the slope in Fig. 6 is expected to be positive in the case of DGA cation. However, with increasing D^{-1} the value of log k_f decreases at higher value of D (78—52) and then increases at lower value of D (52—35). This behavior is explained by the solute-solvent interactions and not by the simple electrostatic law (Eq. 14) nor by the reaction mechanism (Eq. 15). The rate constant, k_f, is equal to $K_{12}k_{23}$ (Eq. 13). The equilibrium constant, K_{12}, is a parameter which denotes the solute-solvent interactions, *viz.*, interactions with the surrounding water molecules. Thus the value of K_{12} gradually decreases with the increase in x_{diox}, *viz.*, decrease in D. If the contribution of the decrease of K_{12} to the value of k_f is larger than that of the increase of k_{23}, the rate constant k_f decreases at higher D where solute-solvent interaction is predominant, and then increases at lower D where the electrostatic effect is predominant.

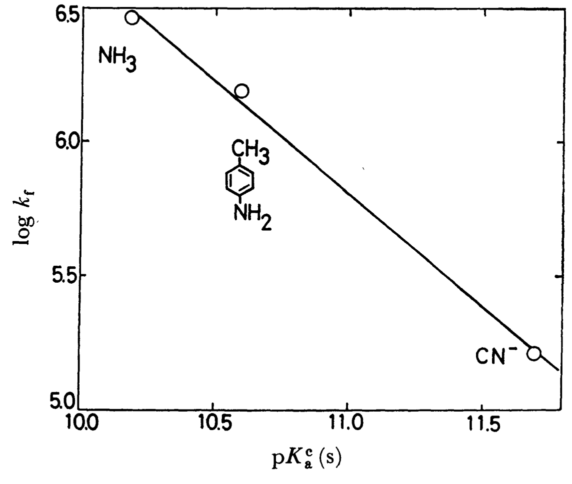

Fig. 7. Plot of log k_f *vs.* pK_a^c(s) in bis(dimethylglyoximato)cobalt(III) complex–OH^- system.

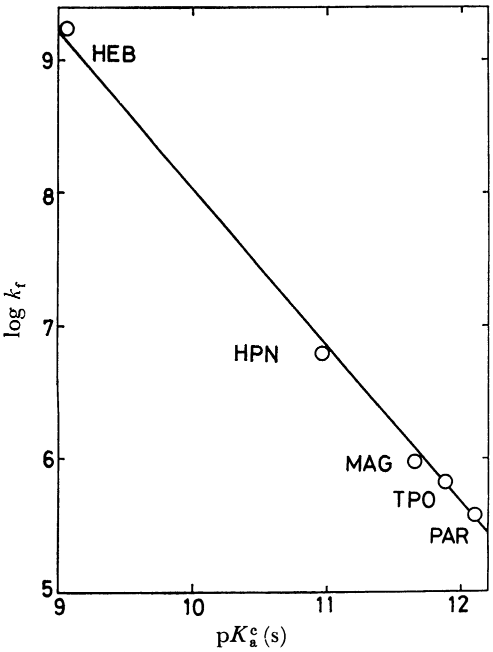

Fig. 8. Plot of log k_f *vs.* pK_a^c(s) in *o*-hydroxy azo compound–OH⁻ system.

Figure 7 shows the Brønsted plot with the slope −0.85 in aqueous solution,

$$\log k_f = -0.85\, pK_a^c(s) + 15.15. \qquad (16)$$

The value is the intermediate one between −0.5 for the substituted malonic acids[27] and −1.2 for *o*-hydroxy azo compounds ($\log k_f = -1.2\ pK_a^c(s) + 20.05$) (Fig. 8).[1-5] Masuda *et al.* reported the relationship of pK_a^c(s) and the basicity of an axial ligand and pointed out the importance of the transmittance of an electronic effect of the axial ligand to the oximato radical.[13] The rate constant k_f does reflect the thermodynamic stability of the intramolecular hydrogen-bond, namely the values of pK_a^c. This fact indicates that the axial ligand with larger electronic effect on the increase in the proton-dissociation of the in-plane oximato group tends to accelerate the dissociation of proton in the intramolecular hydrogen-bond of the Co(III) complex ion.

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22) The absorption in the range 400—500 nm of the base form of DGA cation rapidly increases in the time region of 2 μs div⁻¹. The reciprocal relaxation time of this fast step does not depend on the sum of the equilibrium concentrations of H_2A^+ and OH^- ions at each dioxane content. The signal-amplitude of the fast step depends only on the equilibrium concentration of the base form, HA^0. This indicates that the fast step would be an intramolecular structural change in the base form. The sum of the rate constants, $k_1 + k_{-1}$, for this fast step is determined to be $4.5 \times 10^4 - 2.3 \times 10^5\ s^{-1}$. Since the concentration of the intermediate species accompanied by this fast step is very low, the value of K_a^c(s) is in good agreement with that of K_a^c(k) at each dioxane content.

23) Three relaxation phenomena were observed in the CDG anion–OH⁻ system. The signal amplitude of a very fast step is small as compared with that of DGA cation. The values of $k_1 + k_{-1}$ are found to be 1.3×10^5—$2.0 \times 10^5\ s^{-1}$. The very slow step would be the intramolecular step accompanied by the motion of axial ligands, since the value of τ^{-1} (3—5 s^{-1}) does not depend on the equilibrium concentrations. The values of $k_2 + k_{-2}$ for this slow step are found to be in the range 3.0—5.5 s^{-1}.

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